

BRIEF COMMUNICATIONS

Kinetics of the Reaction between the Active Paste from the Positive Electrode of a Dead Nickel–Iron Battery and Sulfuric Acid

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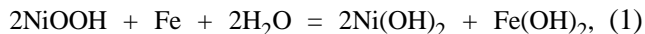
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Abstract—The kinetics of dissolution of a powdered active paste from the positive electrode of a worked-out nickel–iron battery in 0.1 N sulfuric acid at 25, 50, and 75°C was studied by measuring the electrolyte resistance.

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In continuation of previous publications [1, 2], we present the results obtained in studying the reaction between a powdered active paste from the positive electrode of a worked-out nickel–iron (NI) battery and sulfuric acid in the temperature range 25–75°C. The active paste was taken from worked-out NI battery of the TNZh-250-U2 type, the particle size of the powder did not exceed 200 μm.

The overall reaction that occurs in charging and discharge of a NI battery can be represented by the equation:



It follows from this equation that the worked-out active paste from the positive electrode should contain Ni(OH)_2 and NiOOH . An X-ray diffraction analysis revealed graphite and dispersed nickel hydroxide Ni(OH)_2 in the active paste. An X-ray diffraction pattern of the powdered active paste from a worked-out NI battery is shown in Fig. 1.

In hydrometallurgical processing of worked-out electrodes, it is necessary to know the content of sodium or potassium carbonate and hydrocarbonate remaining in pores of the active paste, because their amount affects the expenditure of sulfuric acid for processing of worked-out positive electrodes contain-

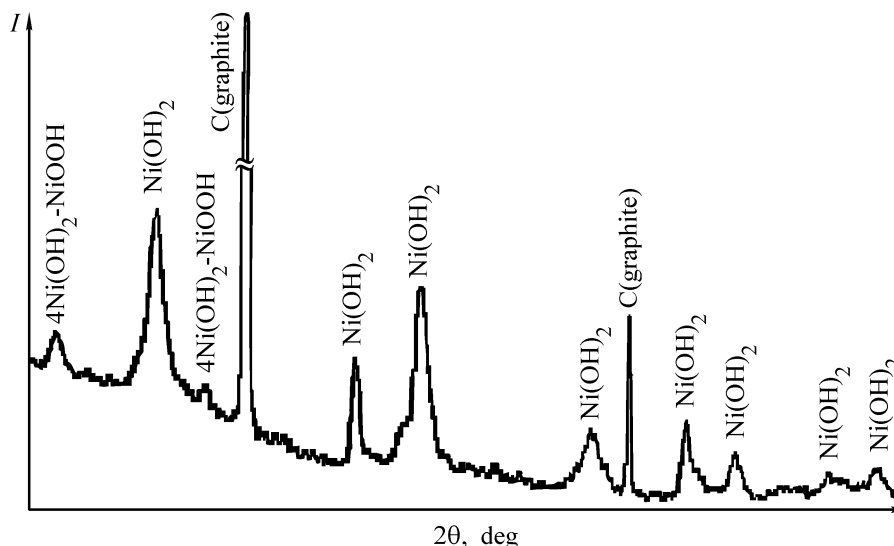


Fig. 1. X-ray diffraction pattern of the powdered active paste from the positive electrode of a worked-out TNZh-250-U2 nickel–iron battery. (*I*) Intensity and (*2θ*) Bragg angle.

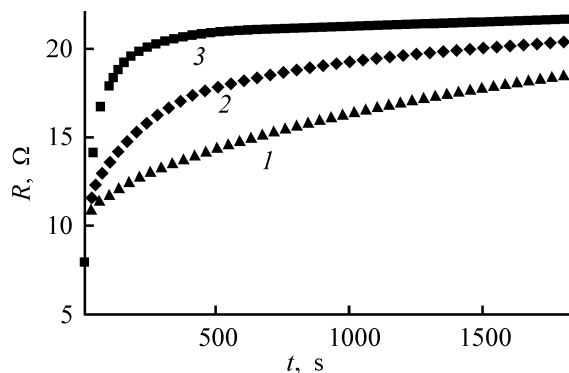


Fig. 2. Variation of the resistance R with time t in dissolution of the powdered active paste from the positive electrode of a worked-out NI battery in 0.1 N sulfuric acid at different temperatures. Temperature ($^{\circ}\text{C}$): (1) 25, (2) 50, and (3) 75; the same for Fig. 3.

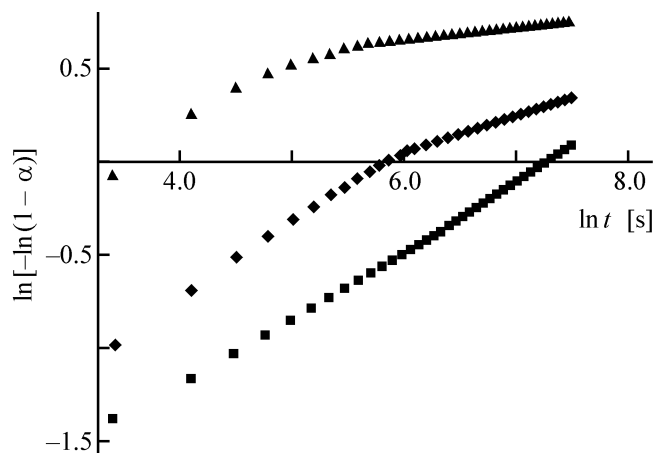


Fig. 3. Dependence of $\ln[-\ln(1 - \alpha)]$ on $\ln t$ in dissolution of the powdered active paste from a worked-out NI battery in 0.1 N sulfuric acid at different temperatures.

ing nickel hydroxide. A conductometric titration showed that, after its prolonged storage in air, the worked-out active paste contains sodium carbonate and hydrocarbonate whose content varies with time. Sodium carbonate is converted into hydrocarbonate, with the result that the content of carbonates in the active paste decreases, and that of hydrocarbonates increases [2].

The kinetics of the reaction of the active paste with sulfuric acid was studied in a thermostated conductometric cell, with vigorous agitation of a solution with magnetic stirrer. Changes in the resistance were measured with an E7-15 immitance meter, with the use of graphite electrodes, during 30 min at intervals of 30 s. The variation of the resistance with time in the course of the dissolution of the powdered

active paste from the positive electrode in a 0.1 N sulfuric acid at 25, 50, and 75°C is shown in Fig. 2.

Two portions can be distinguished in the curve describing the variation of the resistance in dissolution of the active paste from the positive electrode in sulfuric acid. In the first of these, sodium carbonate and hydrocarbonate remaining in the pores of the active paste after its prolonged storage in air are neutralized, and in the second, nickel hydroxide contained in the worked-out active paste reacts with sulfuric acid. The reaction of nickel(II) hydroxide with sulfuric acid results in that the type of charge carriers changes. The rather mobile hydrogen ions are replaced with less mobile nickel ions. As a result, the electrical conductivity of the solution changes in the course of the process [1].

The data obtained were processed using the Erofeev-Kholmogorov equation

$$\alpha = 1 - \exp(-kt^n), \quad (2)$$

where α is the fraction of the reacted substance; k , rate constant; t , time; and n , exponent that accounts for a change in the surface area in the dissolution of the powdered active paste.

The applicability of Eq. (2) can be verified by the existence of a linear dependence $\ln[-\ln(1 - \alpha)] = f(\ln t)$ obtained by twice taking the logarithm of the initial equation. The fact that the curves plotted (Fig. 3) using experimental data are linear shows that the Erofeev-Kholmogorov equation can be used to describe the dissolution kinetics of the powdered active paste from the positive electrode of a worked-out NI battery in sulfuric acid.

Further, the straight lines obtained were processed by the least-squares method to give the value of $\ln k$, from which the rate constant was found by taking the antilogarithm and the activation energy of the process was calculated. The calculation was done using the formula:

$$\Delta E = \frac{RT_1T_2 \ln \frac{k_2}{k_1}}{T_2 - T_1}, \quad (3)$$

where R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and k_1 , k_2 are the rate constants at temperatures $T_1 = 298.15$ and $T_2 = 348.15 \text{ K}$, respectively.

It was found that the neutralization of sodium carbonate and hydrocarbonate occurs in the temperature range $25\text{--}75^{\circ}\text{C}$ in the mixed region ($\Delta E = 23.9 \text{ kJ mol}^{-1}$), and the dissolution of nickel hydrox-

ide in sulfuric acid, in the kinetic region ($\Delta E = 52.7 \text{ kJ mol}^{-1}$).

To determine the degree of nickel recovery from the active paste, a sample was taken after completion of each test, and the content of nickel that passed into solution was determined by titration with Trilon B, as described in [3]. The degree of nickel recovery in dissolution of the powdered active paste from the positive electrode in 0.1 N sulfuric acid at 25, 50, and 75°C was 66, 75 and 88%, respectively.

CONCLUSION

The dissolution of a powdered worked-out active paste from the positive electrode in sulfuric acid

occurs as follows. First, sodium carbonate and hydrocarbonate, and then, nickel hydroxide react with sulfuric acid. The neutralization of sodium carbonate and hydrocarbonate in the range 25–75°C occurs in the mixed region, and the dissolution of nickel hydroxide, in the kinetic region.

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